

Essential aspects of controlling the oxygen content of molten tin in engineering applications



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ABSTRACT

This work investigated issues regarding the control of the dissolved oxygen content of molten tin in engineering applications. It has been shown that the oxygen content of liquid tin can be adequately monitored with commercial, off-the-shelf, ultra-high-impedance electrometers and ceramic oxygen sensors, requiring only minor modifications for use in a liquid metal environment. Hydrogen and argon gases were used to modify and maintain the oxygen content. It was found that the oxygen can be removed from the tin successfully only above about 600 °C in reasonable time, as would be expected from thermodynamics and kinetics. Several scenarios of various ways to handle the tin were investigated, to determine the extent to which one must go in order to maintain a desired oxygen content in molten tin. The electromotive-force and diffusion-coefficient measurements agree reasonably well with the values published in the scientific literature and indicate the range of error to be expected in engineering applications.

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1. Introduction

Metals have historically been melted chiefly in order to re-solidify them into desired shapes. These purposes include the refining of metals and their use for soldering and brazing. In recent decades, though, metals with low melting temperatures have found increasing engineering applications in their molten state, such as for coolants in high-energy transport systems [1]. Lead (Pb) alloys have often been used for these purposes, but tin, which has a melting temperature of 232 °C, is another such candidate material; and unlike lead, tin is not toxic to humans or the environment.

The oxygen content of the liquid metal is an important parameter. On the one hand, too little oxygen in the liquid metal can lead to materials dissolution from the container materials; but on the other hand, too much oxygen can cause system-wide problems. The oxide invariably has a higher melting temperature than the liquid metal and can precipitate out of the liquid metal to free surfaces and onto solid surfaces at cold spots (e.g., heat exchangers in heat transport applications). The oxide can thereby foul heat transfer surfaces and clog pipes and tubes [1].

Alcock and Belford [2] made some of the first experimental measurements of oxygen solubility and reactions in liquid tin, using solid electrolytes. Although much scientific work has been done since then to measure the saturation point and the diffusion coefficient of oxygen in molten tin as functions of temperature, little work has been done regarding the engineering problems of controlling the oxygen content [3,4]. In this work, these problems were investigated in a manner similar to other work done on lead and lead-bismuth-eutectic alloy [1,5]. Off-the-shelf, commercial equipment was used with only minor modifications, and the experiments were conducted on relatively large quantities of tin (many tens of grams). Thus, the engineering knowledge of molten tin has been extended to the laboratory bench-top scale.

2. Method

2.1. Experimental setup

The experimental setup consisted of an oxygen sensor (described below) inserted into a sealed steel container (for environmental control) and with its tip (the active part) submerged in a sample (molten tin) in a ceramic crucible that was at the bottom of the steel container (See Figs. 1 and 2). The steel container was suspended in the center of an electric resistance heater, which could heat the sample to above 700 °C. Thus, this container and heater formed a custom-made autoclave.

Various gases could be injected into the steel container, for controlling the oxygen content of the cover gas and of the sample. To

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Nomenclature

prime (') indicates a quantity at standard chemical activities (but not necessarily at standard temperature)	a_i	chemical activity of substance i
$\Delta_f G_i^{STP}$ standard Gibbs free energy of formation of substance i , at standard temperature and pressure and in standard state	n	the number of electrons exchanged in the chemical reaction (i.e., moles of electrons per mole of product)
$\Delta_f G_i'(T)$ Gibbs free energy of formation of substance i , as a function of temperature (but at standard activities)	F	the Faraday constant (96,485 coulombs per mole of electrons)
$\Delta G(T, a_i, a_j, \dots)$ change in Gibbs free energy, as a function of temperature and chemical activities	$E(T, a_i, a_j, \dots)$	electromotive force, as a function of temperature and chemical activities
c_i chemical concentration of substance i	$E'(T)$	electromotive force, at standard chemical activities, as a function of temperature
	R	the universal gas constant (8.3145 J/mol K)

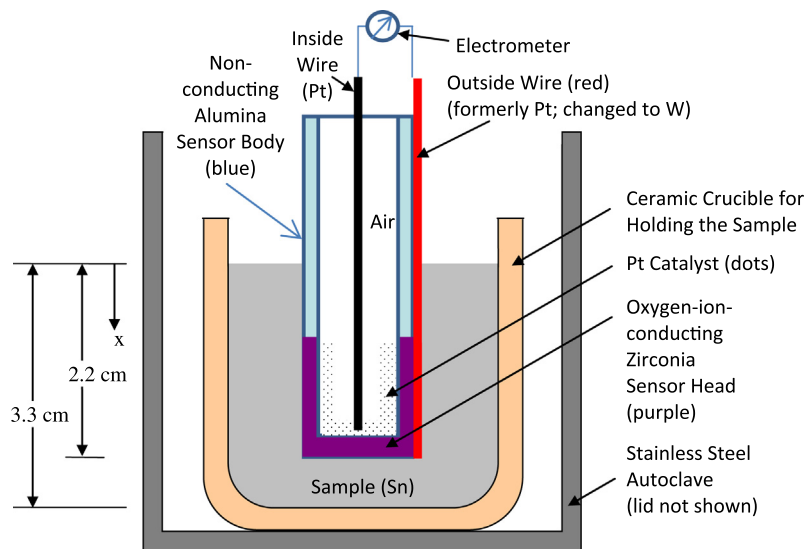


Fig. 1. Schematic of the zirconia oxygen sensor, which uses a Pt–air reference. The indicated dimensions are those from the as-received-Sn and the diffusion experiments, specifically.

obtain a high oxygen environment, the container was supplied with air. For a lower oxygen environment, an inert gas, such as argon, was continuously fed through the container. For a reducing environment, hydrogen was injected. Thus, unlike most of the pre-

vious work on liquid tin [2–4,6], this work controlled the oxygen content with gases and not with electrochemical pumps. Also, unlike experiments using a Sieverts apparatus (e.g., Pehlke and Elliott [7] and Mancha et al. [8]), the oxygen content was controlled by flowing gases, and no vacuum was involved.

The oxygen sensor that was used was a Model DS probe from Australian Oxytrol Systems. This probe consisted of a small zirconia ceramic tip that was joined to a non-conducting alumina ceramic tube with a gas-tight, high-temperature ceramic bond. The zirconia was stabilized with 7 mol percent yttrium oxide (i.e., the tip was yttria-stabilized zirconia, known as YSZ). Because the tip was small, it was possible to completely submerge it in the liquid tin and thereby avoid measuring oxygen from the cover gas. The zirconia ceramic allowed oxygen anions to pass through it but did not appreciably allow electrons or other ions to do so (that is, the electronic conductivity of the zirconia was assumed to be negligible at the temperatures investigated). Therefore, the sensor put out an electromotive force (EMF, voltage) that varied with the difference in the oxygen concentrations between the internal reference of the sensor and the external sample being examined. This EMF was measured with a Keithley 181 nanovoltmeter. A high impedance electrometer was necessary for this measurement because the corresponding current was so small; most typical voltage meters would have let this current leak away and would therefore have measured artificially small EMF values. This issue is discussed further in Section 3.2.

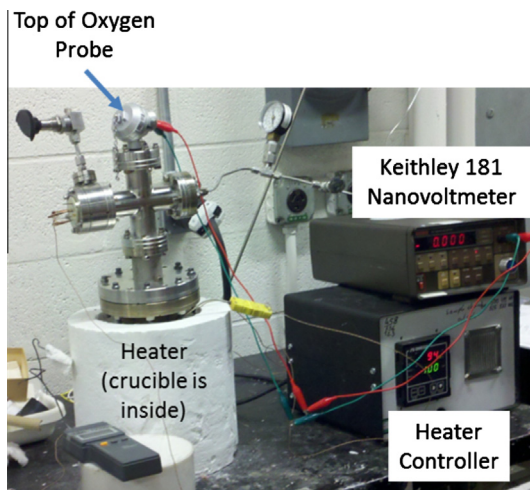


Fig. 2. The experimental setup for using the oxygen probe to measure the oxygen content of tin, under various gas environments.

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